

CHARACTERIZATION OF THE ARGONNE PREMIUM COAL SAMPLES BY PYROLYSIS HIGH RESOLUTION MASS SPECTROMETRY

Randall E. Winans, Robert L. McBeth and Paul H. Neill
Chemistry Division, Argonne National Laboratory, Argonne, IL 60439

INTRODUCTION

The complete set of Argonne Premium Coal Samples have been characterized using Pyrolysis High Resolution Mass Spectrometry (PyHRMS). A major objective in the study is to examine differences in the heteroatom (oxygen, sulfur and nitrogen) containing molecules as a function of rank of the coals. Operating in the high resolution mode makes it possible to directly separate these species from each other and from the hydrocarbon molecules. In addition, many molecules, which can not be observed with gas chromatography by virtue of their size or polarity, can be observed with this method.

We have applied PyHRMS to characterization of separated coal macerals and coal degradation products.¹⁻³ There are many papers on low resolution PyMS applied to coals^{4,5} and one applied to these premium coals.⁶ The PyMS approach can provide very detailed information on the molecules which are released in vacuum pyrolysis, however the probability of secondary reactions is a consideration and all interpretation must be made with this fact in mind. This approach yields more specific molecular data than any other method. A problem with low resolution PyMS is that in many if not most cases there may be several ions present with the same nominal mass but with different chemical compositions. This problem is eliminated by using an high resolution spectrometer which may scan more slowly, but will resolve peaks which overlapped at lower resolution and yield more information.

EXPERIMENTAL

The samples have been obtained from the Argonne Premium Coal Sample Program and the preparation of the samples has been described.⁷ The appropriate elemental analysis for the samples is presented in Table 1. A second set of samples was obtained by extracting the original coals in refluxing pyridine under a nitrogen atmosphere. The residue was washed with dilute aqueous HCl and with methanol and dried *in vacuo* at 60°C.

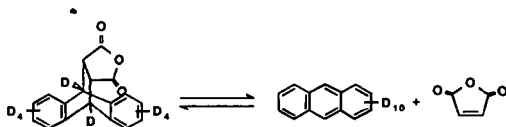
TABLE 1. Elemental Analysis for the Fresh Coal Samples.

Sample	Name	xC(maf)	Per 100 Carbons				Ash
			H	N	S	O	
1	Upper Freeport mvB	85.5	66.0	1.55	0.32	6.59	13.20
2	Wyodak-Anderson SubB	75.0	85.6	1.28	0.23	18.00	8.77
3	Herrin hvCB	77.7	77.2	1.51	1.15	13.03	15.50
4	Pittsburgh hvAB	83.2	76.7	1.69	0.40	7.96	9.25
5	Pocahontas lvB	91.0	58.5	1.25	0.21	2.04	4.23
6	Blind Canyon hvBB	80.7	85.7	1.67	0.17	10.78	4.71
7	Stockton-Lewiston hvAB	82.6	76.3	1.62	0.30	8.93	19.80
8	Beulah-Zap Lignite	72.9	79.5	1.35	0.36	20.88	9.72

Both sets of samples, fresh coal and extract residue, were pyrolysed under the same conditions, in an all glass heated inlet system (AGHIS), rapidly to 600°C. The inlet system was designed in this laboratory to use a quartz pyrolysis probe fitted with a platinum grid which was heated by a computer controlled DC power supply. The inlet system was thermostated at 300°C and a silicon-carbide leak metered the sample into the mass spectrometer. An internal standard has been used which was the Diels-Alder adduct of D¹⁰-anthracene and maleic anhydride prepared from the two reactants in refluxing p-xylene. The spectrometer, a Kratos MS-50, was operated at 40,000 dynamic resolving power scanning at 100 sec/decade, with an EI source set at 70 eV. The resulting data (10 scans) were averaged and sorted according to heteroatom content and hydrogen deficiency (Z number = number of double bonds + rings).

RESULTS AND DISCUSSION

The internal standard is very important for comparing the results of the PyMS between the different rank coals. It allows a more quantitative comparison, while ideally not participating in any secondary reactions. Our standard appears to function very well. The Diels-Alder product shown below undergoes a thermally induced retro-reaction very cleanly at approximately 300°C to yield D¹⁰-anthracene quantitatively. In the precise mass measurement mode it is easy to separate this ion from the coal pyrolysis products. All of the data presented in this paper have been normalized to this standard. Since this standard is



released at a lower temperature than the coal pyrolysis there is no evidence for deuterium scrambling. The peaks resulting from the standard are excluded from the final averaged spectra and from the Z number and heteroatom analysis. In the analysis the following heteroatoms or combination of heteroatoms were searched for: none, oxygen, two oxygens, three oxygens, sulfur, two sulfurs, sulfur-oxygen, sulfur-nitrogen, and nitrogen. Typically, peaks accounting for greater than 90% of the total ion current can be assigned reasonable formula. This approach has been used to characterize petroleum and coal liquids and has recently been described in detail.⁸

A typical averaged spectra is shown in Figure 1 for the fresh Illinois Herrin Seam coal (APCS #3). Note that there are a significant number of peaks at m/z ratios greater than 200, which is characteristic for all the high volatile bituminous coals. Hydrocarbons are usually found in the 400 region which can be attributed to molecules derived from pentacyclic triterpenoids. This is especially true in the Utah coal (APCS #6) which is rich in lipinites. Most of these types of molecules are extractable, which is seen in the loss of these high mass peaks in the pyridine extracted Utah coal.

The effect of pyridine extraction on the distribution of pyrolysis products is very rank dependent. There is very little difference between raw and extracted coals for those of higher rank such as the low volatile bituminous coal, while

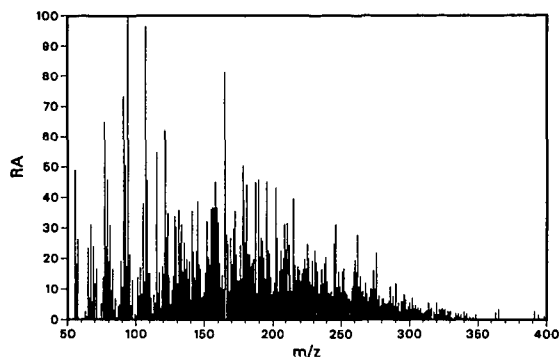


Figure 1. Averaged mass spectra for the fresh Herrin Seam coal (APCS #3), [RA = relative abundance].

an increased yield of pyrolysis products and a greater variety of molecules is found for the lower rank coals which have been extracted. The results for the subbituminous coal are shown in Figure 2. Also, note that the higher mass peaks (>200) are more abundant in the extracted sample. This effect may be simply due to the fact that the low rank coals contain a significant amount of water.

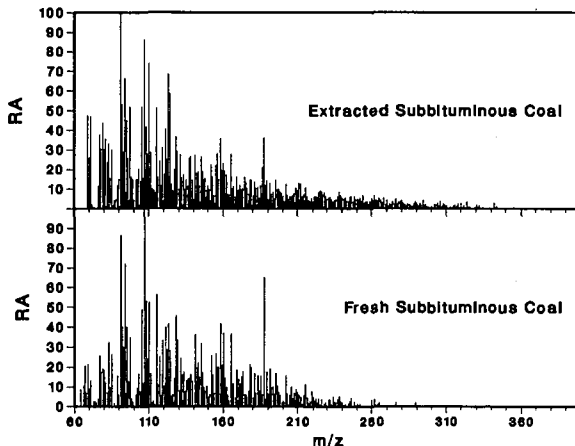


Figure 2. Comparison between averaged mass spectra for fresh and extracted subbituminous coal (APCS #2).

The analysis of the as received sample indicated 28% moisture for the subbituminous coal. The pyridine extraction will effectively remove this water and the sample was vacuum dried. The effect of vacuum drying on the fresh samples is being explored.

The oxygen content of these coals greatly varies from 20% in the lignite down to 2.5% in the lv bituminous. However, the relative yields of oxygen containing species in the pyrolysis product does not change as much as one would

expect based on this variation in oxygen content. There is a decrease with rank which can be seen in the adjacent Figure 3. Also, species with two oxygens are almost absent in the higher rank coals, the mv and lv bituminous ranks. It is known that for lignite and subbituminous coals significant amounts of the oxygen is lost as CO and CO₂.⁹ However, it may be possible that in the higher rank coals the pyrolysis products are enriched in the oxygen containing molecules while the residue is depleted compared to the original oxygen content. These coals have not been exposed to atmospheric oxygen making it unlikely that these oxygen containing aromatics were formed from surface oxidation.

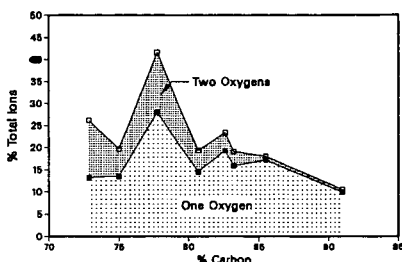


Figure 3. Variation in the oxygen containing products as a function of carbon content presented in a stacked plot.

Although the total amount of oxygen-containing species in the products does not change dramatically with rank, the types of molecules that are seen do change with rank. As can be seen in the adjacent Figure 4, the amount of ions in single ring aromatics (Z=4) decreases with increasing rank while the larger heteroaromatics such as dibenzofuran (Z=9) and naphthobenzofuran (Z=12) are more prevalent in the higher rank coals. These compounds are likely assignments for a combination of these Z numbers and the carbon number for the first peak seen in the series with one oxygen. For example, while hydroxyfluorene has a Z number of 9, the parent molecule has a carbon count of 13 which is one greater than dibenzofuran. Presently, a method is being used to help to distinguish between hydroxylated aromatics and both aryl ethers and annellated furans by modifying the acidic hydroxyls prior to pyrolysis.² With the Pocahontas low volatile bituminous coal, molecules with a single oxygen were observed at up to Z=19 with significant abundances at up to Z=17. With the lignite coal the maximum hydrogen deficiency observed was 12.

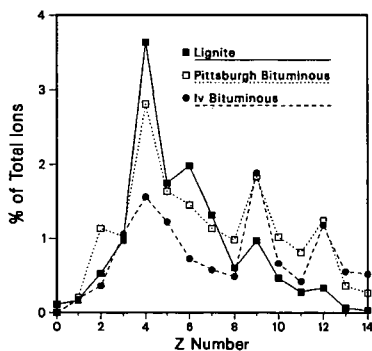


Figure 4. Distribution of molecules which contain one oxygen as a function of hydrogen deficiency for three coals.

Examination of the data from molecules containing a single sulfur yielded two very interesting results for the higher rank coals. Data from the very sulfur-rich Illinois Herrin Seam coal are compared to those from the low volatile bituminous coal in Figure 5. First, the yield of sulfur in the low volatile coal seems to be enhanced in comparison to the original amount of sulfur in the coal. The hv bituminous coal has five times as much, 'organic' sulfur in it as the low volatile coal. The yield of H_2S is probably much larger for the Herrin Seam coal. Second, in the Pocahontas coal small amounts of thiophene(Z=3) and dibenzothiophene(Z=9) are observed. These species along with benzothiophene and naphthobenzothiophene are typical sulfur heterocyclics found in coal liquefaction products^{10,11} and coal extracts.^{11,12} However, in duplicate experiment for both the fresh and extracted sample, the most abundant class of sulfur compounds had a Z number of 10 as is seen in Figure 5 and a carbon number of 14 for the parent molecule in the series. This result was also observed in the Upper Freeport mv bituminous coal. Selected peaks for the Herrin coal and the Pocahontas low volatile coal are shown in

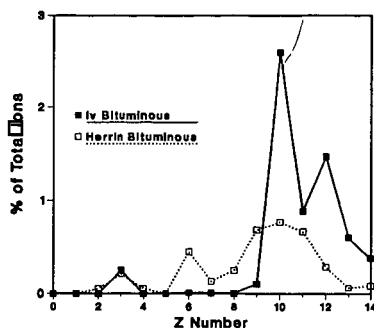


Figure 5. Distribution of species containing a single sulfur atom for two of the fresh coals.

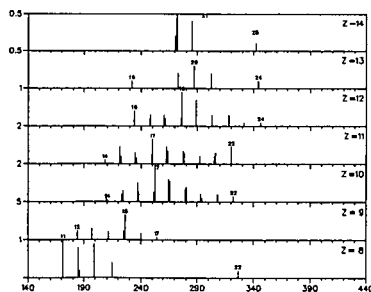


Figure 6. Selected ion peaks containing one sulfur from Z = 8 - 14 for the Herrin seam coal.

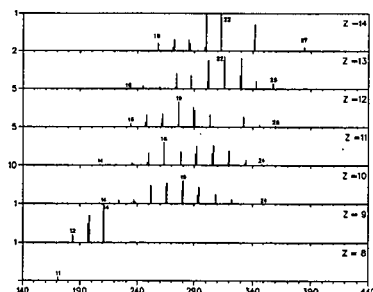


Figure 7. Selected ion peaks with one sulfur for Z = 8 - 14 for the Pocahontas low volatile coal (APCS #5).

Figures 6 and 7. Note that in both these plots the relative abundances for each subplot will vary since they are automatically scaled. The numbers on each plot represent the carbon number for the adjacent peak. In Figure 7 the most abundant peak has 19 carbons and a hydrogen deficiency of 10. A possible structure which would fit this data is alkylated phenylbenzothiophene. Phenylthiophenes have been identified in the extracts of Wyoming coal (PSOC-521).¹¹ The position of the phenyl group would determine if fragmentation would result in benzothiophene fragment peaks which are not seen in the high rank coal. The benzothiophene

fragment is observed if the phenyl were on the thiophene ring.¹³ Another possibility, although it seems less likely, is an addition of a 5-member ring to dibenzothiophene which one would expect to be converted to an indene type structure in the pyrolysis. The results are being investigated further using PyGCMS for these high rank coals.

SUMMARY

Extraction of the coals yielded variable results ranging from enhanced pyrolysis yield from the low rank coals to no difference for the very high rank coal. It was shown that this approach is useful for examining the distribution of heteroatom containing molecules which are produced in the vacuum pyrolysis. It is interesting to note that these species appear to be enriched in the products produced from the higher rank coals.

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REFERENCES

1. Winans, R.E.; Hayatsu, R.; Scott, R.G.; McBeth, R.L. In *Chemistry and Characterization of Coal Macerals*; Winans, R.E.; Crelling, J.C., Eds.; ACS Symposium Series No. 252; American Chemical Society: Washington, D.C. 1984; pp. 137-155.
2. Winans, R.E.; Scott, R.G.; Neill, P.H.; Dyrkacz, G.R.; Hayatsu, R. *Fuel Proc. Tech.* 1986 12, 77-88.
3. Winans, R.E.; Hayatsu, R.; McBeth, R.L.; Scott, R.G.; Botto, R.E., *Preprints, Div. Fuel Chem., ACS* 1988, 33(1), 407-414.
4. Melcalf, G.S.; Windig, W.; Hill, G.R.; Meuzelaar, H.L.C. *Int. J. Coal Geol.* 1987, 1, 245-268.
5. van Graas, G.; de Leeuw, J.W.; Schenk, P.A. In *Advances in Organic Geochemistry* 1979; Douglas, A.G.; Maxwell, J.R., Eds.; Pergamon Press: Oxford, 1980; pp. 485-493.
6. Yun, Y.; Hoesterey, B.L.; Meuzelaar, H.L.C.; Hill, G.R., *Preprints, Div. Fuel Chem., ACS* 1987, 32(4), 301-308.
7. Vorres, K.S.; Janikowski, S.K., *Preprints, Div. Fuel Chem., ACS* 1987, 32(1), 492-499.
8. Schmidt, C.E.; Sprecher, R.F.; Batts, B.D. *Anal. Chem.* 1987, 59, 2027.
9. Serio, M.A.; Solomon, P.R.; Yu, Z.Z.; Deshpande, G.V.; Hamblen, D.G., *Preprints, Div. Fuel Chem., ACS* 1988, 33(3), 91-101.
10. Nishioka, M.; Lee, M.L.; Castle, R.N. *Fuel* 1986, 65, 390-396.
11. Nishioka, M. *Energy Fuels* 1988, 2, 214-219.
12. White, C.M.; Douglas, L.J.; Perry, M.B.; Schmidt, C.E. *Energy Fuels* 1987, 1, 222-226.
13. Blatt, H.; Brophy, J.J.; Colman, L.J.; Tairych, W.T. *Aust. J. Chem.* 1976, 29, 883-890.